Supporting Information for VOC emissions during the usage of benzalkonium chloride and quaternary ammonium compound-based disinfectants

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Section S1. Description of commercial products

CP#1: "multipurpose antibacterial cleaner"

- 0.086% alkyl (67% C_{12}, 25% C_{14}, 7%C_{16}, 1% C_8-C_{10}-C_{18}) dimethyl benzyl ammonium chloride
- .0216% alkyl (50% C_{14}, 40%C_{12}, 10% C_{16}) dimethyl benzyl ammonium chloride
- Full ingredient list (accessed 7/20/22):

Ingredient	Purpose	CAS
BAC	Antimicrobial, active ingredient	63449-41-2; 68424-85-1
Water	Diluent	7732-18-5
Pneoxyisopropanol	Solubilizer	770-35-4
Lauramine Oxide	Surfactant	1643-20-5
Ethanolamine	pH control	141-43-5
Fragrances		
2-Methyl-3-(P-Isopropylphenyl) propionaldehyde		103-95-7
2-Sec-Butylcyclohexanone		14765-30-1
Benzyl salicylate		118-58-1
Decanal		112-31-2
Dimethylcyclohex-3-Ene-1-Carbaldehyde (Isomer Unspecified)		27939-60-2
Ethyl 2-methylbutyrate		7452-79-1
Ethylene brassylate		105-95-3
gamma-decalactone		706-14-9
L-menthol		2216-51-5
Methylbenzyl acetate		93-92-5
Propylene glycol		57-55-6
Terpineol acetate		8007-35-0
Tetrahydrolinalool		78-69-3

CP#2: "disinfectant cleaner"

- 0.034% alkyl (50% C_{14}, 40% C_{12}, 10% C_{16}) dimethyl benzyl ammonium chloride
- 0.026% octyl decyl dimethyl ammonium chloride
- 0.013% dodecyl dimethyl ammonium chloride
- 0.013% dioctyl dimethyl ammonium chloride

CP#3: "'24 hour' multipurpose cleaner"

- 0.200% alkyl (50% C_{14}, 40% C_{12}, 10% C_{16}) dimethyl benzyl ammonium chloride
- 0.150% octyl decyl dimethyl ammonium chloride
- 0.075% dodecyl dimethyl ammonium chloride
- 0.075% dioctyldimethyl ammonium chloride
- Full ingredient list (accessed 7/20/22):

Ingredient	Purpose	CAS
BAC	Antimicrobial, active ingredient	68424-85-1
Quaternium-24	Antimicrobial, active ingredient	32426-11-2
Didecyldimonium chloride	Antimicrobial, active ingredient	7173-51-5
Dimethyldioctylammonium chloride	Antimicrobial, active ingredient	5538-94-3
Water	Diluent	7732-18-5
Dipropylene Glycol Butyl Ether	Solvent	29911-28-2
Polyethyloxazoline	Binder	25805-17-8
C9-C11 parethione	Surfactant	68439-46-3
Triethanolamine	pH adjuster	102-71-6
Dipropylene glycol	Fragrance	25265-71-8; 110-98-5
Ethylene Brassylate	Fragrance	105-95-3
2,6-dimethyl-7-octen-2-ol	Fragrance	18479-51-1 ; 18479-58-8
Hexyl cinnamal	Fragrance	101-86-0; 165184-98-5

CP#4: "bacteriostatic antimicrobial sanitizing spray"

- 0.54% 3-trihydroxysilylpropyl octadecyl dimethyl ammonium chloride
- 0.900% 1-decanaminum, N-dycyl, N-N-dimethyl chloride

Section S2. Vocus calibration

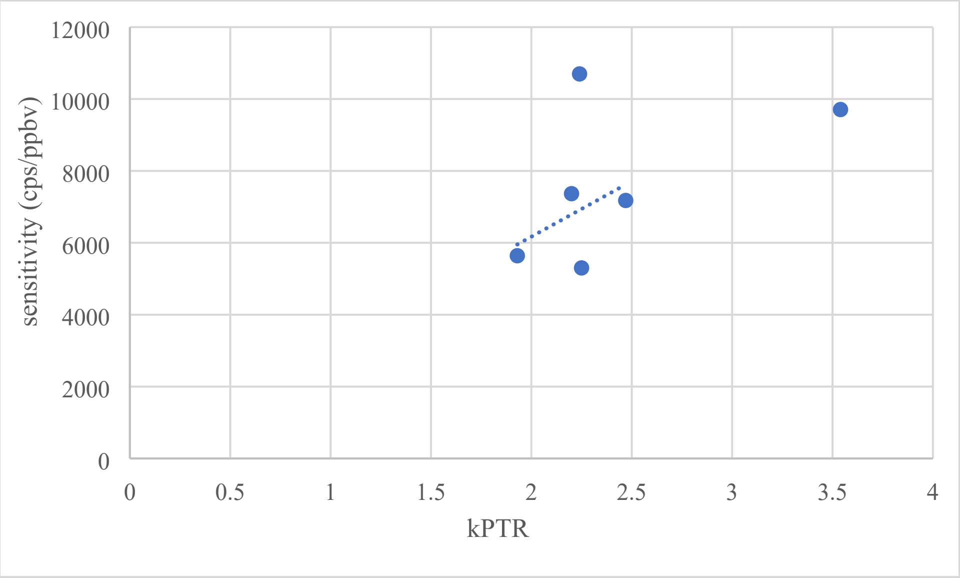

Figure S1. Calibration curve constructed for the Vocus. Calibrants are benzene (k_{PTR} = 1.93); styrene (k_{PTR} = 2.24); m-xylene (k_{PTR} = 2.2); acetophenone (k_{PTR} =3.54); p-isopropyltoluene (k_{PTR} = 2.25); and limonene, alpha-pinene, beta-pinene, and 3-carene grouped together as monoterpenes (k_{PTR} = 2.47). Acetophenone is taken as the sum of C8H8OH+ and C6H7O+; p-isopropyltoluene is taken as the sum of C10H15+ and C7H9+; and monoterpenes are taken as the sum of C10H17+ and C6H9+. Fragmentation patterns are based on those previously described in Pagonis et al. (2019).[1]

Blank chamber experiment injection

A blank chamber injection experiment was performed where the misting device was filled with deionized water and injected into the chamber as in the other experiments. Traces showing the relative humidity (RH) and selected VOC ion signals are shown below in Figure S1. VOCs are selected based on those signals that were also observed during BAC solution injection.

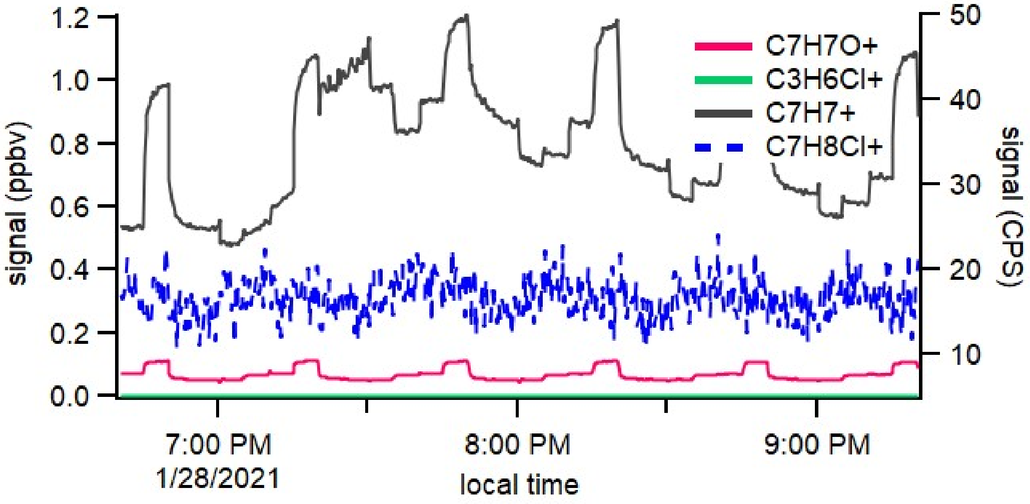

Figure S2. Relevant ion signals observed during the "blank" water droplet injection. $C_7H_8Cl^+$ is plotted on the right axis in terms of counts per second (CPS), as no signal is observed for this ion. No changes are observed in $C_7H_7O^+$ or $C_3H_6Cl^+$ signals while a minor increase is observed for C_7H_7+.

Section S3. Measurements on the $C_7H_7^+$ ion

To explore the origin of the $C_7H_7^+$ ion observed during chamber and headspace sampling under the Vocus operating conditions described in the main text (E/N ratio ~150 Td), we performed headspace measurement of several solutions containing potential source molecules. Solutions were made with 0.10 mL of pure analyte in 10 mL of deionized water. Analytes tested were purchased from Millipore-Sigma and were benzyl chloride (#185558, 99%), benzyl alcohol (#108006, 99%), and benzyl amine (#185701, 99%).

Analyte ion ratios stabilized after ~30 seconds, and this period was used to calculate ion ratios. Ions used were based on signals that were observed to increase during headspace measurements and product ions that have been observed in prior work following H_3O^+ clustering and proton transfer.[1]

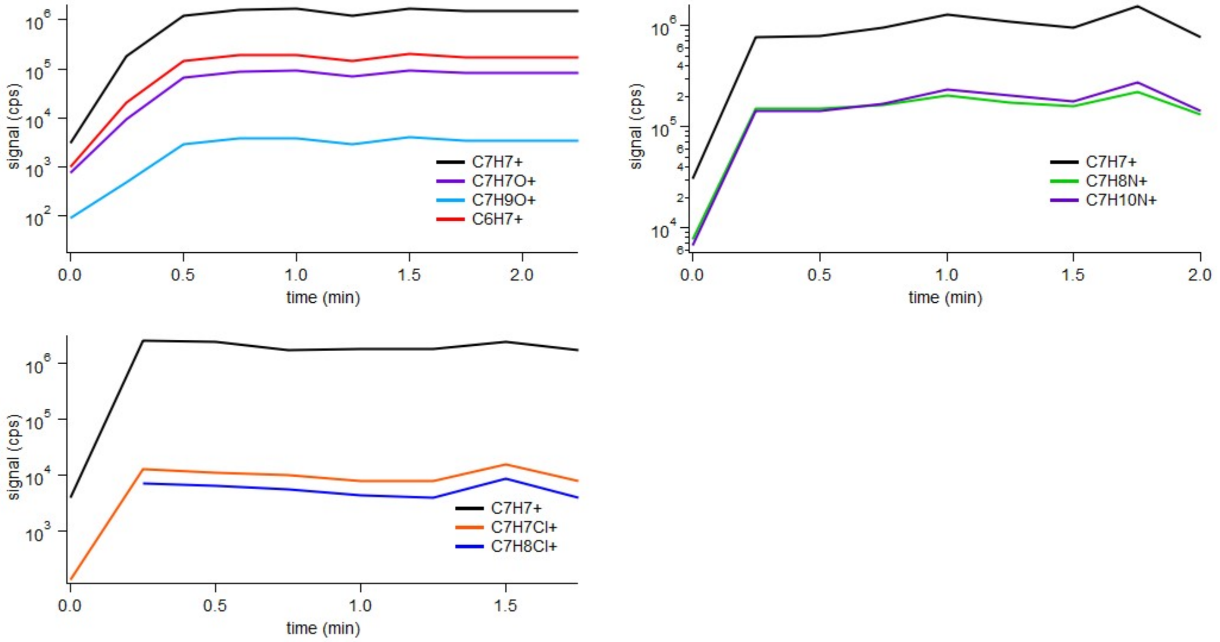

Figure S3. Ion traces observed during headspace sampling of benzyl alcohol (upper left), benzyl amine (upper right), and benzyl chloride (lower left) solutions. Benzyl alcohol is primarily detected as $C_7H_7^+$ (loss of H_2O, ~85%), $C_6H_7^+$ (loss of CH_2O, ~10%), and $C_7H_7O^+$ (loss of H_2, ~5%). Benzyl amine is primarily detected as $C_7H_7^+$ (loss of H_3N, ~74%), $C_7H_8N^+$ (loss of H_2, ~13%), and $C_7H_{10}N^+$ (~13%). Benzyl chloride is primarily detected as $C_7H_7^+$ (loss of H_2Cl, >99%) with <1% detected as $[C_7H_7Cl]H^+$; $C_7H_7Cl^+$, likely resulting from O_2^+ charge transfer, is also observed and is included to demonstrate the detection of this ion (as also discussed in the main text).

Section S4. Mass balance and calculation of emission factors

Concentrations of VOC analytes are calculated using a mass balance approach based on prior work.[2] Periods of stable VOC concentrations (comprising measurements at ~40, 70, and 100 minutes elapsed, as shown in Figure 2) were used for calculations. During these periods VOC injection rate was closely balanced against VOC loss due to air change. The air change rate per hour (ACH) was measured to be 2.3 hr^{-1} prior to chamber injection. VOC mass concentrations in the chamber at each time point were calculated by converting the measured VOC concentrations from ppbv to $g\ L_{air}^{-1}$ by assuming vapor density of an ideal gas (Equation 1) and then accounting for VOC loss due to air change and VOC accumulation within the chamber (Equation 2). Background chamber concentrations measured prior to the start of injection were subtracted from the measured $C_{chamber}$ value used in Equation 2. The mass emitted was then used to calculate an emission rate (Equation 3), which was then used to calculate the total mass concentration in the original solution based on the injection duration of ~110 minutes (Equation 4).

$$\rho_{ideal}(g\ L^{-1}) = \frac{P * (Molar\ Mass)}{R * T} \qquad \text{(Equation 1)}$$

$$Mass_{emitted} = (ACH * chamber\ volume)\int_{0}^{t}(C_{chamber} - C_{inflow})dt + V\int_{0}^{t} dC_{chamber} \qquad \text{(Equation 2)}$$

$$E_t = \frac{M_{emitted}}{time\ elapsed} \qquad \text{(Equation 3)}$$

$$M_{total} = E_t * (injection\ duration) \qquad \text{(Equation 4)}$$

Table S1. Analyte concentrations displayed in terms of $g_{analyte}$ per $kg_{product}$. Measured densities were 0.995 g/mL for Sigma BAC, 0.996 g/mL for CP#1, and 0.996 g/mL for CP#2.

	Sigma BAC (g/kg)	CP#1 (g/kg)	CP#2 (g/kg)	CP#3	CP#4
$C_3H_8N^+$	1.3E-4 (n/a)	2.6E-3 (Y)	4.2E-5 (Y)	Y (n/a)	n/a (Y)
$C_3H_6Cl^+$	6.8E-4 (n/a)	N (N)	N (N)	N (n/a)	n/a (N)
$C_3H_6ClO^+$	3.4E-4 (n/a)	7.5E-5 (N)	N (N)	N (n/a)	n/a (Y)
$C_6H_7^+$	8.8E-3 (n/a)	0.19[1] (Y)	6.0E-4 (Y)	Y (n/a)	n/a (Y)
$C_6H_7O^+$	1.6E-3 (n/a)	1.4[1] (Y)	Y (Y)[2]	Y (n/a)	n/a (Y)
$C_7H_7^+$	0.058 (n/a)	0.23 (Y)	5.2E-3 (Y)	Y (n/a)	n/a (Y)
$C_7H_7O^+$	8.4E-3 (n/a)	1.5[1] (Y)	2.5E-4 (Y)	Y (n/a)	n/a (Y)
$C_7H_{10}N^+$	3.3E-4 (n/a)	9.6E-5 (Y)	1.5E-4 (Y)	Y (n/a)	n/a (Y)
$C_7H_9O^+$	Y (n/a)	Y (Y)	Y (Y)	Y (n/a)	n/a (Y)
$C_7H_8Cl^+$	2.9E-4 (n/a)	8.5E-4 (Y)	2.1E-4 (Y)	Y (n/a)	n/a (Y)

$C_7H_7Cl_2^+$	1.4E-4 (n/a)	N (Y)	N (Y)	N (n/a)	n/a (Y)

[1] calculation not feasible because background air concentrations could not be accurately determined
[2] attribution to another specific molecule is possible as discussed in main text

Section S5. Detection of large saturated amines

Several ion signals are observed during injection of CP#1 that likely originate from large amines with the formulas $C_{14}H_{31}N$ and $C_{16}H_{35}N$, consistent with the BAC precursors N,N-dimethyl dodecylamine and N,N-dimethyl tetradecylamine. These species are practically nonvolatile and condense to an extent within the unheated sampling lines used during this work, complicating quantitation of the airborne concentration. We instead show below the average mass spectrum at m/z 214 (corresponding to ($C_{14}H_{31}NH^+$) at the inside-chamber valve position before injection and approximately two hours after injection (Figure S4) to illustrate the increase in this signal. The average $C_{14}H_{32}N^+$ concentration over this interval is approximately 75 ppt. These species are detected primarily as protonated adducts with a smaller contribution from the deprotonated ion. Tertiary amines (i.e., amines lacking an H bound to N) have been detected as deprotonated ions in prior work.[1] Other large (C11-C17+) saturated amines are not observed, consistent with the C14 and C16 amines (62% and 30%, respectively) comprising the bulk of the BAC in CP#1, according to the ingredients label. We note that the C12 BAC species that comprises 67% of the first BAC ingredient list entry would be synthesized from a C14 amine because of the two methyl groups.

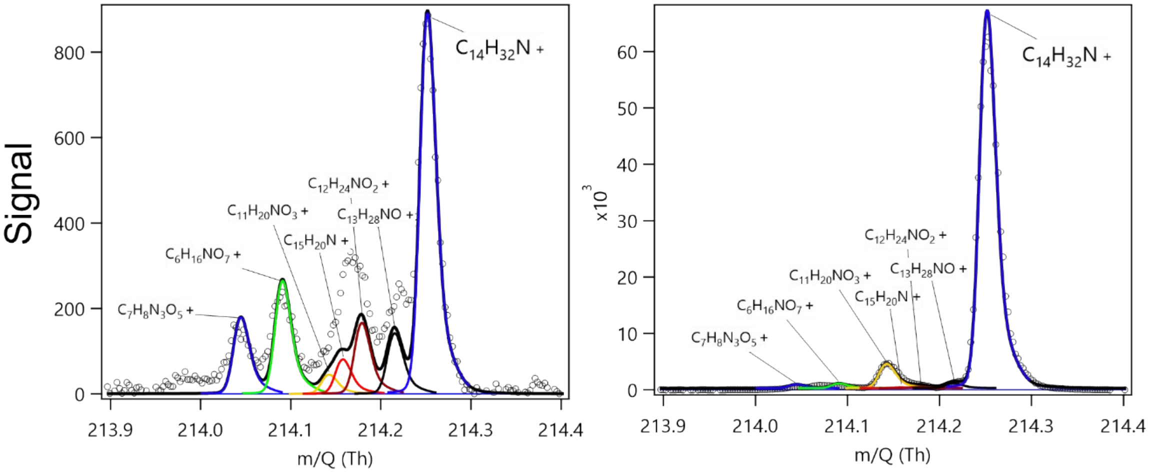

Figure S4. 4-minute average mass spectra at the inside-chamber position before CP#1 injection (left) and approximately two hours after injection began (right). Note the difference in y-axis scale between the two images.

Section S6. PTR measurements of D3 cyclic methyl siloxanes

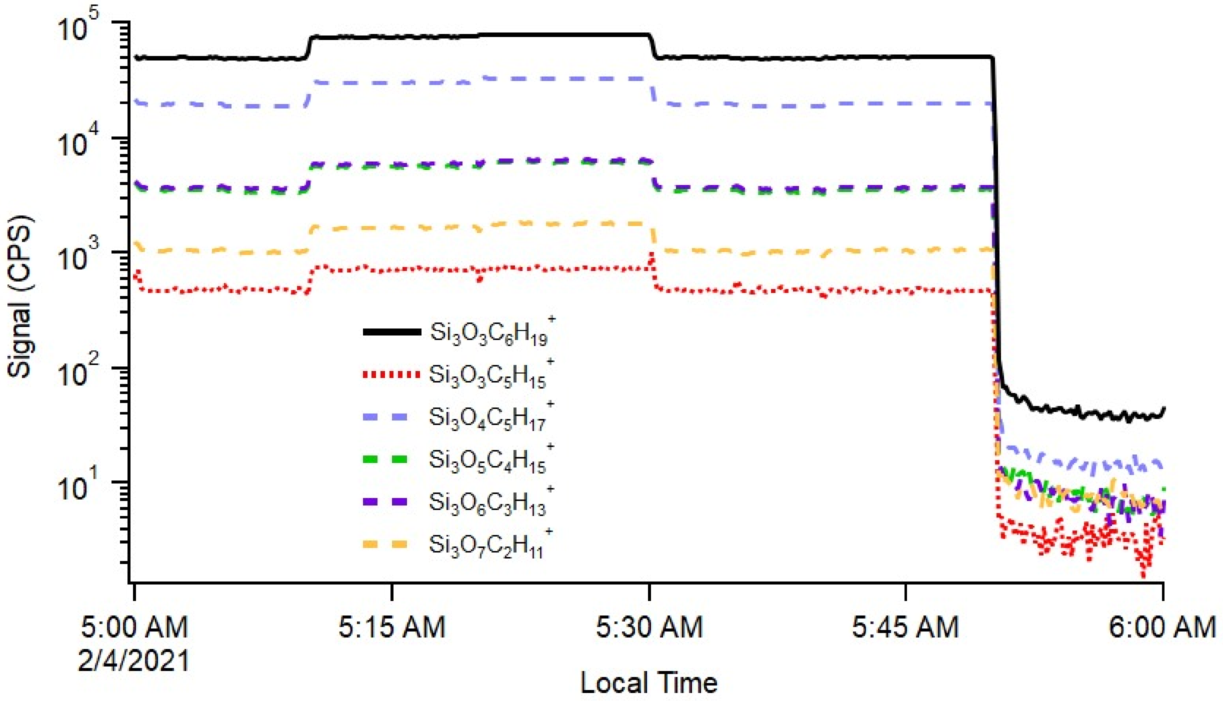

Figure S5. Timeseries of D3 trimethylcyclosiloxane and associated reaction product ions observed during Vocus calibration at the operating conditions described in the main text (E/N ratio ~150 Td). The base protonated ion is shown in the solid black trace, an ion reflecting net loss of CH_4 is shown in the dotted red trace, and ions produced through successive net loss of CH_2 and addition of O, potentially reflecting replacement of a CH_3 group by OH during water clustering, are shown in the multicolored dashed traces. The side reactions that occur during reagent clustering and analysis of the D3 siloxane shown here will not necessarily be reflective of the processes that would occur with other organo-Si analytes but show that a variety of side reactions may be possible.

References

(1) Pagonis, D.; Sekimoto, K.; de Gouw, J. A Library of Proton-Transfer Reactions of H3O+ Ions Used for Trace Gas Detection. *J. Am. Soc. Mass Spectrom.* **2019**, *30* (7), 1330–1335. https://doi.org/10.1007/s13361-019-02209-3.

(2) Tang, X.; Misztal, P. K.; Nazaroff, W. W.; Goldstein, A. H. Volatile Organic Compound Emissions from Humans Indoors. *Environ. Sci. Technol.* **2016**, *50* (23), 12686–12694. https://doi.org/10.1021/acs.est.6b04415.